

In Situ DGT Sensing of Bioavailable Metal Fluxes to Improve Toxicity Predictions for Sediments

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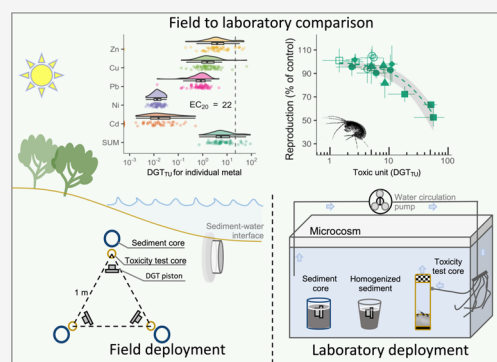
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ABSTRACT: An increased risk of adverse biological effects of metals in sediments may be accompanied by high labile metal fluxes as measured by the diffusive gradients in thin films (DGT) technique. To improve the usefulness of the DGT technique for sediment quality risk assessments, we used the simpler and more cost-effective piston DGTs rather than planar DGT probes to measure bioavailable metal fluxes in naturally contaminated sediments with widely varying composition (properties, metals and concentrations) and assessed their prediction of toxicity to amphipod reproduction in a flow-through microcosm. DGT pistons were deployed in sediments under different conditions, both in the field (in situ) and in the laboratory in sediment cores (lab-equilibrated) and in homogenized sediments (lab-homogenized). We demonstrated that the metal flux toxic units, DGT_{TU} , measured in situ best predicted the magnitude of toxicity to amphipod reproduction. For sediments that had been highly disturbed before testing, DGT_{TU} were less predictive for observed toxicity, but the copper flux alone (DGT_{TU-Cu}) was effective, indicating copper was the primary cause of toxicity in these highly perturbed sediments. Overall, our study highlighted that the adverse effects induced by excessive bioavailable metals in contaminated sediments can be consistently sensed by the DGT pistons.

KEYWORDS: labile metal fluxes, bioavailability, chronic toxicity prediction, line of evidence, sediment quality assessment, benthic organisms



1. INTRODUCTION

The diffusive gradients in thin films (DGT) technique has become popular for determining concentrations of labile metals within sediments.^{1,2} When deployed in sediments, the DGT device accumulates metals present in the porewater including the weakly bound metals released from sediment particles by diffusion, and provides a measure of the time-integrated labile metal fluxes.³ Through measurement of a combined pool of labile metals, this technique has been applied for the purpose of assessing the metal exchange at the sediment water interface^{3–6} (whether sediments are acting as a sink or source), potentially bioavailable concentrations,^{7–9} as well as the risk of toxicity to benthic organisms exposed to metal-contaminated sediments.^{10–14} Multiple studies have observed that increasing concentrations of DGT-labile metals correlate with increasing bioaccumulation,^{15–19} and that toxic effects thresholds based on DGT-induced metal flux measurements provide better predictions of risk than total sediment metal concentrations^{11,13,14} or other solid-phase extraction measures.¹²

For the purpose of sediment quality assessment and management decisions,^{20,21} the premise is that sediments with higher DGT-labile metal fluxes have a higher risk of causing adverse effects to benthic organisms, and that practical thresholds for excessive bioaccumulation and toxic effects can

be derived from DGT measurements. However, the evidence linking higher DGT–metal fluxes to greater biological uptake and effects have been primarily drawn from studies in the laboratory under well controlled conditions, despite DGTs being highly amenable to in situ use. To enable the DGT technique as an effective line of evidence for assessing the risk of excessive bioavailable metal exposure and sediment toxicity, there is a major need to optimize its application in the field.^{22–24} It is well recognized that changes to metal bioavailability within sediments may occur during field sediment collection, and from homogenization or other disturbances before chemical or biological tests.^{5,10,25–29} The overlying water conditions in the laboratory cannot be entirely matched to those existing in the field, resulting in significant differences in labile metal concentrations in overlying waters.^{30–33}

A further concern for the use of DGT as a routine line of evidence is the cost-effectiveness.³⁴ While “planar” DGT

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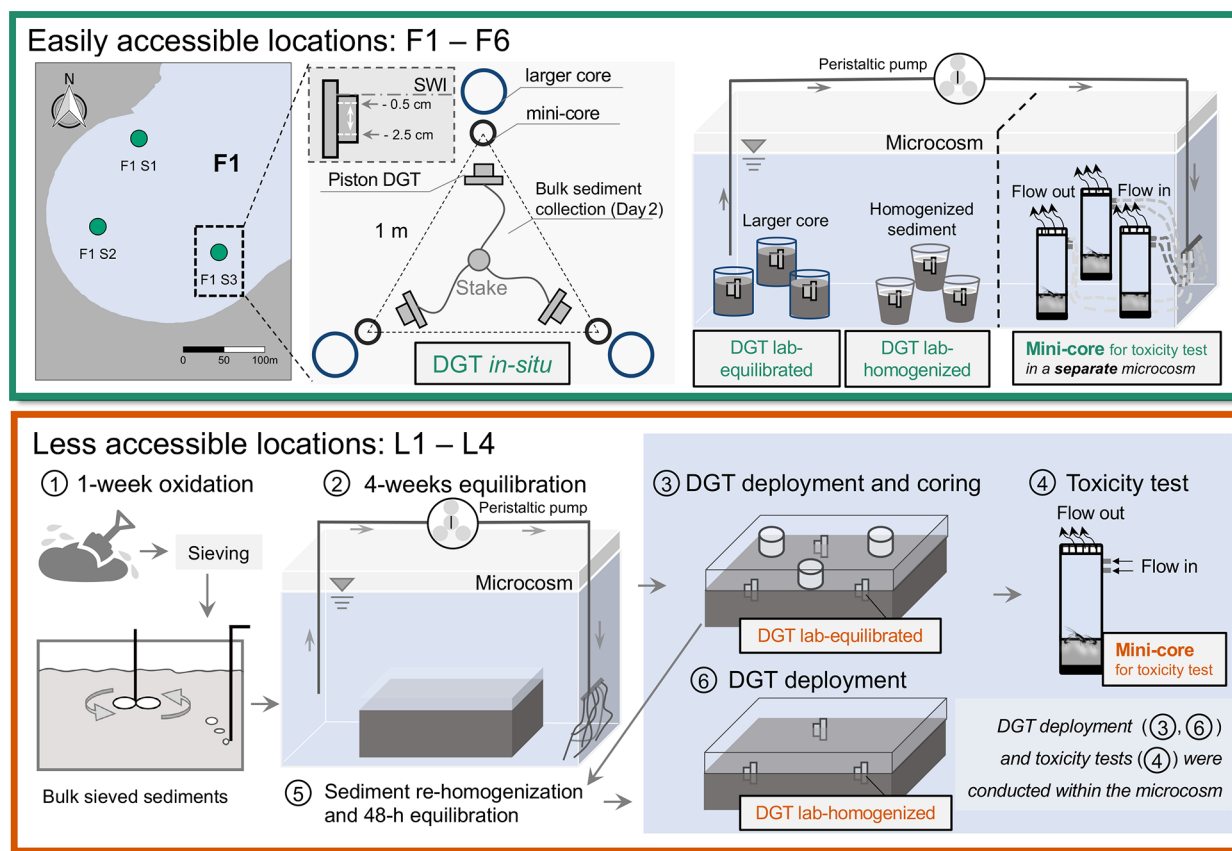


Figure 1. Deployment of DGT pistons and toxicity test setup for different type of sediments. For easily accessible locations (F1–F6, in green frame), DGT pistons were deployed in three scenarios: field in situ, lab-equilibrated, and lab-homogenized; triplicate mini-cores with preserved sediment structure were also taken for toxicity tests. At less accessible locations (L1–L4, in orange frame), bulk sediment was collected and treated by 1-week oxidation and 4-weeks equilibration; DGT pistons were then deployed in two scenarios: lab-equilibrated and lab-homogenized; triplicate mini-cores were also taken in equilibrated sediments for toxicity test. Photos are provided in the SI.

probes (rectangular geometry, $\sim 2.5 \text{ cm} \times 16 \text{ cm}$ measurement surface) have generated DGT–metal flux data that provide strong dose–response relationships for predicting metal toxicity to benthic organisms,^{11,13,16,35} these probes are considerably more expensive and require more technical expertise to section before analyses than “piston” DGT probes (circular geometry, referred to as DGT piston hereafter).³⁶ The planar DGT probes enable measurement of porewater depth profiles of metal concentrations and/or fluxes,^{1,2} but this detail may not be necessary for assessments if the risks of toxic effects are well predicted by the DGT-induced metal fluxes within a few cm of the sediment–water interface (SWI).^{11,13}

In this study, we assessed differences in metal fluxes measured by DGT samplers deployed in the field (in situ) and in the laboratory, both in minimally disturbed or equilibrated sediment cores and in intensively homogenized sediments. The DGT-labile metal fluxes were then used to predict toxicity to the reproduction of a benthic estuarine-marine amphipod, *Melita plumulosa*, which is recognized for its sensitivity when exposed to bioavailable metals.^{11,37–39} To improve the practicality of methods and findings from the present study, metal fluxes were measured using much simpler and more cost-effective DGT pistons while toxicity effects to amphipod reproduction were assessed within a microcosm under flow-through conditions to achieve metal concentrations in overlying waters reasonably similar to those expected in the field. Further, the study was applied across naturally

contaminated sediments from 10 locations that had a wide range of properties and metal contamination histories.

2. MATERIALS AND METHODS

2.1. Sediment Collection and Experimental Design.

Ten estuarine-marine locations (Figure S1, Supporting Information (SI)) were selected, among which sediments displayed a wide range of metal contaminants (concentrations and mixtures), varying sediment properties, and low concentrations of organic contaminants.^{40–42} Six of the locations (F1–F6) provided easy access to sediments in shallow water (15–30 cm water depth at low tide), which was necessary for the in situ DGT deployment and collection of intact sediment cores. The other four locations were either covered by high densities of oysters (L1–L3, still with shallow water depth) or had a water depth $>3 \text{ m}$ (L4), and both conditions prevented collection of adequate sediment cores and/or in situ DGT deployments, and therefore bulk sediments were collected and tested entirely in the laboratory. At the nine shallow-water locations (F1–F6, L1–L3), three or four sites were selected along the shore, and for the deep-water location a single site was selected.

From the combined design, we were able to assess the performance of DGT–metal flux measurements in predicting metal toxicity for three different DGT deployment scenarios: field-in situ, lab-equilibrated, and lab-homogenized. Details are also provided in SI Section S1 and S2 of the in situ DGT

piston deployment and retrieval, collection of intact sediment cores and bulk sediments, and homogenization and oxidation-equilibration treatments.

In brief, within locations F1–F6 (18 sites in total, SI Table S2), at each of the sites, on Day 1, the DGT deployment (in situ) and intact sediment core collection were conducted in triplicate with a distance of 1 ± 0.2 m apart as an equilateral triangle (Figure 1 and SI Figure S2). At the vertexes of the triangle, DGT pistons were deployed, and two intact sediment cores were taken from within 10–20 cm of the in situ DGT pistons for laboratory DGT deployment (10 cm diameter lab-equilibrated cores, >10 cm sediment depth) and for toxicity tests (5.5 cm diameter mini-cores, ~4 cm sediment depth). On Day 2, the DGT pistons were retrieved (after 24 h) and surficial sediments were collected from the center of each triangle area (~6 kg of bulk surficial sediments from 0 to 5 cm depth). Both types of the sediment cores (mini-cores and lab-equilibrated cores) were placed separately in laboratory microcosms (110-tank) and 100 L of seawater added to submerge the core tops. The mini-cores for toxicity tests were equilibrated for a week in microcosms before the tests commenced on Day 8. To concurrently measure the metal fluxes in bulk homogenized sediments, also commencing on Day 8, the bulk surficial sediments were homogenized (lab-homogenized sediments) in 500 mL polycarbonate beakers and placed into the same microcosm containing lab-equilibrated cores, and probes were deployed on Day 10 in both sediments simultaneously for 24-h and retrieved on Day 11.

For the less accessible locations L1–L4 (11 sites in total, SI Table S2), surficial sediments (0–5 cm depth) were collected and press-sieved through a 2 mm plastic mesh to remove larger debris (rock, shells). The homogenized bulk sediment collected from these locations were highly anoxic in appearance (black with sulfide smell). This was attributed to enhanced biodeposition of organic rich sediments by oysters,^{43,44} and minimal sediment resuspension occurring in these locations because sediment movement was restricted by the presence of hard substrates (oyster beds and rocks). In sulfidic sediments the metals Cd, Cu, Ni, Pb, and Zn are predominantly bound as metal sulfide phases that exhibited low metal bioavailability.^{45–47} Sediment disturbance through bioturbation by benthic organism and hydrodynamic resuspension processes introduces oxygen into sediments and can increase the bioavailability of some metals,^{25,48,49} and it was decided that partially oxidized surface sediment with potentially higher concentrations of bioavailable metals were desirable for this study. A partially oxidized sediment was created by mixing these anoxic sediments with aerated seawater multiple times over a week before they were placed in containers (27 cm length \times 18 cm width \times 17 cm depth) to equilibrate for additional 4 weeks while submerged in the microcosm (Figure 1). For these oxidized and then equilibrated sediments, on Day 1, DGT pistons were deployed, and on Day 2 the DGTs were retrieved (lab-equilibrated). Cores were then taken for toxicity tests, and the sediments remaining were thoroughly mixed (similar to collecting the bulk sediment for F1–F6) and probes were also deployed 48-h after rehomogenization (lab-homogenized) (Figure 1). To minimize sediment resuspension during deployment and retrieval of DGTs and during sediment core collection, the seawater in the microcosm was drained and replaced with clean seawater following the operations.

2.2. DGT Application and Data Analysis. Commercially available Chelex-DGT pistons (purchased from DGT Research Ltd.) were deployed to measure labile metal fluxes in the surficial sediments. A typical DGT piston sampler assembles a filter membrane, a porous diffusive gel, and a Chelex binding layer into a circular plastic holder that comprises an o-shape cap and a piston-shaped bottom base.⁵⁰ When deployed vertically in the sediment, with the upper edges of the samplers level with the SWI (Figure 1, SI Figure S2h), it provides a consistent flux measurement within the depth from 0.5 to 2.5 cm below the SWI (exposure area = 3.14 cm²) (Figure 1).

Prior to use, these DGT samplers were deoxygenated in 0.05 M NaCl solution (purified by Chelex-100 grains) for at least 4 h and transported under nitrogen atmosphere to the deployment locations (field and laboratory). They were then inserted vertically into the sediment until a depth that their upper edges buried 1–2 mm into the sediments. After a 24 h deployment, the DGT pistons were retrieved, rinsed with deionized water to remove sediments deposited on the surface, and transferred individually in clean plastic zip bag back to the laboratory where they were refrigerated (4–6 °C) until time of analysis. Within a month of retrieval, these DGT samplers were disassembled, and the metal-binding layer was then digested in 1 mL of 1 M HNO₃ solution (Baseline, Seastar Chemical) for 24 h as described previously.⁵¹ The eluent was diluted using 2% HNO₃ solution and Mn, Fe, Cu, Zn, Ni, Cd, and Pb concentrations determined by inductively coupled plasma-mass spectrometry (8800 Triple Quad ICP-MS, Agilent Technologies) with a range of QA/QC procedures described below and in SI Section S5.3, Table S1).

For quality control, 16 blank DGT pistons were also subject to the same operational procedures except deployment in sediments for both field and laboratory DGT applications. The metal concentrations of these blank DGT pistons were also determined. The equivalent metal fluxes, assuming a 24 h deployment, measured in these blank DGTs were <0.5 $\mu\text{g}/\text{m}^2/\text{h}$ for Mn, Cu, Ni, and Pb, <0.02 $\mu\text{g}/\text{m}^2/\text{h}$ for Cd, and <20 $\mu\text{g}/\text{m}^2/\text{h}$ for Fe, all of which were substantially lower than the majority of metal fluxes found in deployed DGT pistons. Zinc was consistently detected at a level of 14 ± 8 $\mu\text{g}/\text{m}^2/\text{h}$, accounting for 2–100% (with a mean of 33%) of the zinc fluxes measured in the blank DGTs. Metal fluxes measured in all deployed DGT pistons were corrected by subtracting the fluxes measured in the corresponding batch of blank DGT pistons.

2.3. Toxicity Tests. To mimic the field environment, where metals released from the sediments will disperse and dilute within the overlying water, the toxicity tests were conducted in the mini-cores that operated as flow-through exposure chambers held within a large volume of a microcosm (Figure 1c) as described by Zhang et al.³⁰ The mini-core chambers (Perspex cylinders, 550 mL, 5.5 cm diameter, and 23 cm height) that contained sediment cores collected from the field (F1–F6) and laboratory (L1–L4), were submerged in 100 L seawater within the microcosm (110 L, 52 cm length \times 42 cm width \times 52 cm height) (Figure 1). The seawater was circulated through the chambers at a flow rate of 240 mL/min, taking it from the top of the microcosm and pumping through ports into the exposure chamber and allowing it to exit via nylon mesh (180 μm pore size) at the top (Figure 1). The chambers had another port for the introduction of food during the test.

Toxicity to reproduction of the amphipod, *M. plumulosa*, was assessed following a 10 day exposure to the sediments (SI

Section S4), and reported as % of control sediments.^{11,20,30,38} This amphipod species lives in a benthic environment, burrows, and deposit feeds in surficial sediments. During a 10 day exposure, a female amphipod typically undergoes two reproductive cycles and produces two broods. At the end of the exposure, surface sediments (<1 cm depth) were sieved using a 180 μm sieve, and the number of juveniles retained and the embryos carried by females were counted to calculate the reproduction.

Toxicity tests of contaminated sediments were conducted concurrently with a control test using the control sediment (a relatively uncontaminated sandy sediment). For quality assurance, the series of toxicity tests were only considered acceptable when 6–16 juveniles per female organism were found in the concurrent control test was found.³⁰ The reproduction end point was then calculated by dividing the number of offspring (embryos and juveniles) produced in each toxicity test chamber with the number of survived female amphipods, and expressed as a percentage of controls. Toxicity to reproduction was detected when the reproductive output was less than 85% of the control at a significance of $p < 0.05$ (student's t test).

2.4. Sampling and Chemical Analysis. Sediment analyses included particle size distribution ($\% < 180 \mu\text{m}$), total organic carbon (TOC), acid-volatile sulfide (AVS), total recoverable metals (TRM; aqua regia digestion), dilute-acid extractable metals (AEM; 1 M HCl), and polycyclic aromatic hydrocarbons (PAHs). The methods for collecting, handling and the analyses of sediments and waters have been described previously and are summarized in the SI. A range of other contaminants exist in the sediments (e.g., organochlorine pesticides, polychlorinated biphenyls (PCBs), mercury) but their concentrations rarely exceeded sediment quality guideline values (SQGVs) and should not contribute any toxicity effects to the amphipod reproduction.^{40,52,53}

2.5. Data Analysis. DGT pistons accumulate metals from pore waters including the labile metal species desorbed from solid phases during deployment. This fraction of metals is most simply expressed as a DGT-induced metal flux.^{1–3} Although it is possible to calculate a DGT-labile metal concentration, this concentration is operationally defined and is influenced by the resupply rate of metals to pore waters (released from sediment particles) that needs to be estimated.⁴ For this reason, we present the DGT measurements as fluxes, and for the purpose of the toxicity risk assessment, these DGT–metal fluxes ($\mu\text{g}/\text{m}^2/\text{h}$) were further divided by the corresponding water quality guideline values (WQGVs) (Cu, Pb, Cd, Zn, and Ni: 1.3, 4.4, 5.5, 15, and 70 $\mu\text{g}/\text{L}$, respectively, while ignoring the differences of the units)⁵⁴ to derive the number of toxic units for individual metals and then as sum of toxic units DGT_{TU} .

3. RESULTS AND DISCUSSION

3.1. Sediment Characteristics. The sediments from 29 sites at 10 locations showed large variations in physical and chemical properties (SI Table S2). The $<180 \mu\text{m}$ particle size fraction varied from 7.4 to 99% and TOC from 0.6 to 15%. The sediments were contaminated by a wide range of metals (concentrations and mixtures), with 66% of the sites having a TRM concentrations exceeding the SQGV²⁰ for Cu (65 mg/kg), 90% for Zn (200 mg/kg), 21% for Ni (21 mg/kg), 90% for Pb (50 mg/kg), and 38% for Cd (1.5 mg/kg). Redox conditions in sediments also varied, with 21% of the sites

showing an undetectable amount of AVS in sediments ($<0.5 \mu\text{mol}/\text{g}$), 27% with 10–40 $\mu\text{mol}/\text{g}$, and 14% with $>40 \mu\text{mol}/\text{g}$. Considering the AVS and TOC concentrations, the concentration of metals would be predicted to represent a low risk of toxicity for at least a third of the sediments.⁴⁵ The concentrations of total PAHs ranged from 2.6 to 39 mg/kg and were below concentrations that cause toxicity to the amphipod reproduction ($<20 \text{mg}/\text{kg}$ 1% OC, when normalized to 1% of OC).⁵³

3.2. DGT–Metal Fluxes. Labile metal fluxes measured in deployed DGT pistons under different scenarios followed a consistent order of $\text{Fe} > \text{Mn} > \text{Zn} > \text{Cu} \geq \text{Pb} > \text{Ni} > \text{Cd}$ (SI Figures S3 and S4). The magnitude of the DGT–metal fluxes is influenced by the concentration of labile metals present in porewaters and available for release from sediment particles. The observation that the DGT–Cu and Pb fluxes were greater than the DGT–Ni flux, despite partition coefficients for Cu and Pb typically being greater than Ni,⁵⁵ reflects the generally much greater concentrations of Cu and Pb than Ni in the sediments (SI Table S2). Significant correlations were observed between the magnitude of the fluxes of the different metals, but the level of correlation varied under different levels of disturbance (SI Figure S5). DGT–Cu, Zn, Ni, and Pb fluxes measured in situ were significantly correlated ($p < 0.05$) (SI Figure S5a); a moderate level of disturbance caused by collecting and transferring sediment cores to the laboratory and deployment under laboratory conditions did not reduce the significance of correlations between these metals (SI Figure S5b); but a higher level of disturbance by sediment homogenization changed the correlation pattern, resulting in the absence of correlation between Cu–Ni and Ni–Pb (SI Figure S5c).

When compared to sediments in situ, the laboratory cores and homogenized sediments had increasing degrees of disturbance that were expected to influence metal fluxes.^{2,56} The mean DGT–Fe fluxes were significantly greater ($p < 0.05$) and the distribution range of the data narrower with increasing level of disturbance (in situ $<$ laboratory-cores $<$ lab-homogenized) (SI Figure S3). There are a number of factors that may contribute to the differences; including, the direct disturbances caused by homogenizing sediments that mixed the redox-stratified porewater and solid-phase constituents^{29,57} and the different equilibration periods before DGT piston deployment in the laboratory, and potentially reduced overlying water flow above DGT in laboratory cores within the microcosms that may suppress porewater transport and hyporheic exchange with the overlying water compared to DGT in the field location.^{58–62} All these processes appear to favor the development of more reducing conditions within the surface sediments, where Fe(III)-(hydr)oxides in the oxidized layer of the sediment cores and at all depths within homogenized sediments may then be reductively released as Fe(II) into porewater and accumulated by DGT.^{2,63} When considering the whole data set, there were not significant differences in DGT–Mn fluxes, although the redox processes of these two metals in the surface sediments are closely linked. A reducing environment in sediments may promote the release of metals from Fe(III)-(hydr)oxide phases as they dissolve under mildly reducing conditions⁶³ (SI Figure S4) and precipitation of metal sulfide solid phases when conditions favor sulfate reduction.^{64,65} We observed inverse correlations between DGT–Fe fluxes and fluxes of Cu, Zn, and Pb in lab-equilibrated and lab-homogenized scenarios, whereas such

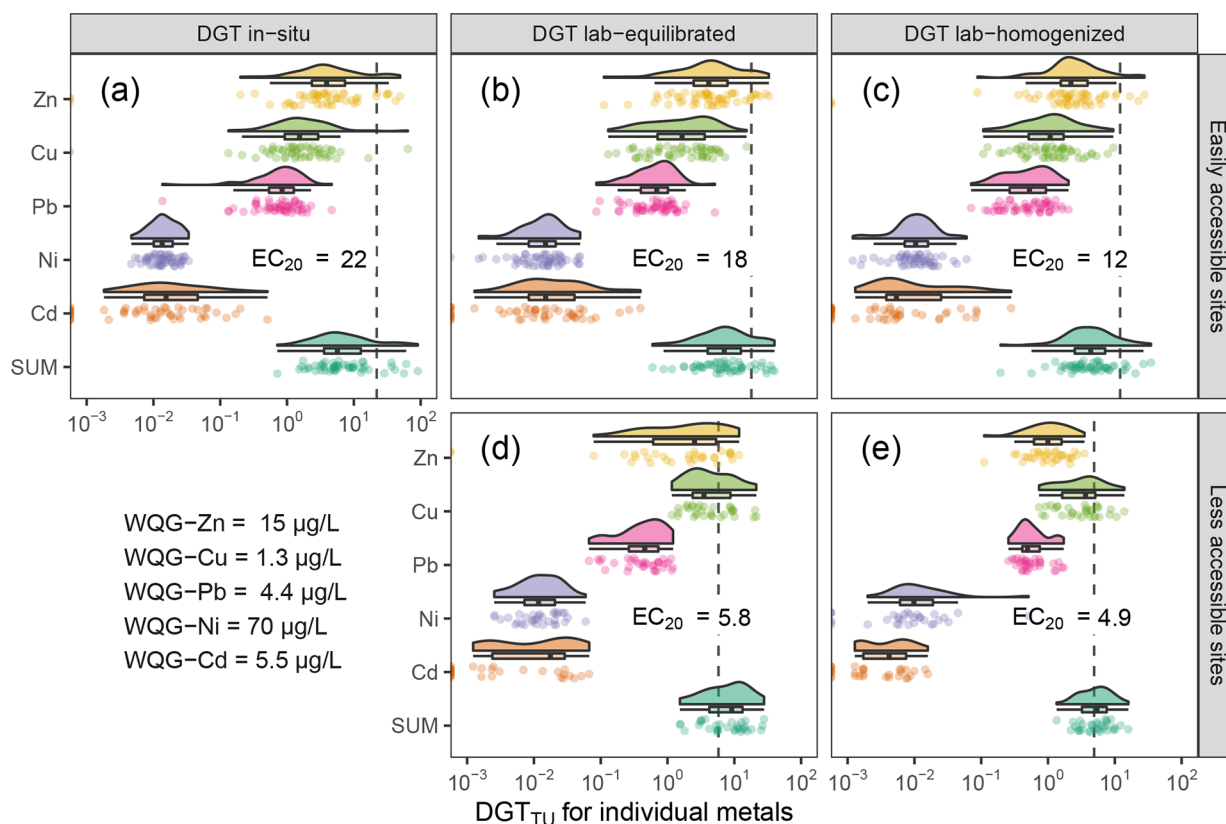


Figure 2. Metal flux toxic units for individual metals and the sum (DGT_{TU}). DGT–metal fluxes were normalized to the corresponding water quality guideline values (WQGVs, bottom left panel), as described in the methods. Each raincloud plot combines a probability density function of DGT_{TU} values, a boxplot providing statistical inferences, and scattered data points of these values.⁷⁰ The vertical dashed lines represent the 20% effect concentrations (EC₂₀) derived from the overall DGT_{TU}–toxicity relationship (c.f. section 3.3).

correlations were absent for the in situ scenario (SI Figure S5a,b,c). Overall, this indicated labile metal fluxes changed as a result of sediment disturbance, which may influence the DGT–metal flux–toxicity relationship in different deployment scenarios.

For the sediments that underwent the oxidation and equilibration treatment, metal fluxes measured in the L1–L4 sediments also exhibited significant correlations between DGT–metal fluxes of Zn, Ni, and Pb (SI Figure S5d). However, DGT–Cu was not correlated with these three metal fluxes, suggesting its unique behavior during oxidation and equilibration. The behavior of copper in sediments is likely affected by a combination of processes, with the partitioning between sediment and porewater influenced by its speciation, oxidation, and reduction kinetics, and affinity for different particulate phases.^{5,57,66} The process of rehomogenization further disturbed the equilibrium that was established in sediments, and no metal fluxes were correlated, except for the Mn–Cd pair (SI Figure S5e).

3.3. Application of DGT–Metal Fluxes to Predict Toxicity. The toxicity of metals differs between metals and organisms, with copper being the most toxic (of Cd, Cu, Ni, Pb, and Zn) to most estuarine–marine organisms (WQG–Cu = 1.3 µg/L),⁵⁴ and also highly toxic to the amphipod.^{11,67} Normalizing DGT–metal fluxes to the corresponding WQGVs and summing as total toxic units has shown its usefulness in predicting the toxicity of metals in sediments to the amphipod.¹¹ The DGT_{TU} values for the individual metals and the toxic unit sum is compared for the DGT piston deployment scenarios in Figure 2. In undisturbed sediments

from easily accessible locations (F1–F6, Figure 2a–c), Cu, Pb, and Zn contributed most to the DGT_{TU} sum (28 ± 16%, 13 ± 9%, and 58 ± 20%, respectively) while Ni and Cd contributed minimally (<1%). In the highly disturbed sediments from less accessible locations (L1–L4, Figure 2d,e), copper contributed 63 ± 20% to the DGT_{TU} sum, compared to Pb (11 ± 7%), Zn (26 ± 20%), and <1% for Ni and Cd. Considering the combined toxicity of the different metals, while recognizing potential differences in the toxic unit approach owing to different modes of action of different metals,^{46,47} the F1–F6 series would be predicted to be less toxic than the L1–L4 series of sediments (i.e., lower EC₂₀ in Figure 2). In relation to the different contribution of metals to the DGT_{TU} sum, the oxidation and equilibration treatments (L1–L4) had a proportionally greater contribution from copper.

Despite the large differences in the physical and chemical properties of sediments from different sites, strong metal exposure (dose)–toxicity relationships existed between the DGT_{TU} and toxicity measured in intact sediment cores (Figure 3a–c). In general, similar relationships existed for different DGT piston deployment scenarios (in situ, lab-equilibrated, and lab-homogenized), but the DGT pistons deployed in situ provided the clearest relationship. Amphipod reproduction was not significantly different from controls until a metal flux value of ~10 (DGT_{TU}) was exceeded. Above the DGT_{TU} threshold of 10, reproduction decreased with increasing DGT_{TU}. Overall, the consistent trends between amphipod reproduction and DGT_{TU} measured in different scenarios demonstrated the ability of DGT–metal fluxes to predict risk of chronic toxicity of these metals in sediments. However, there were important

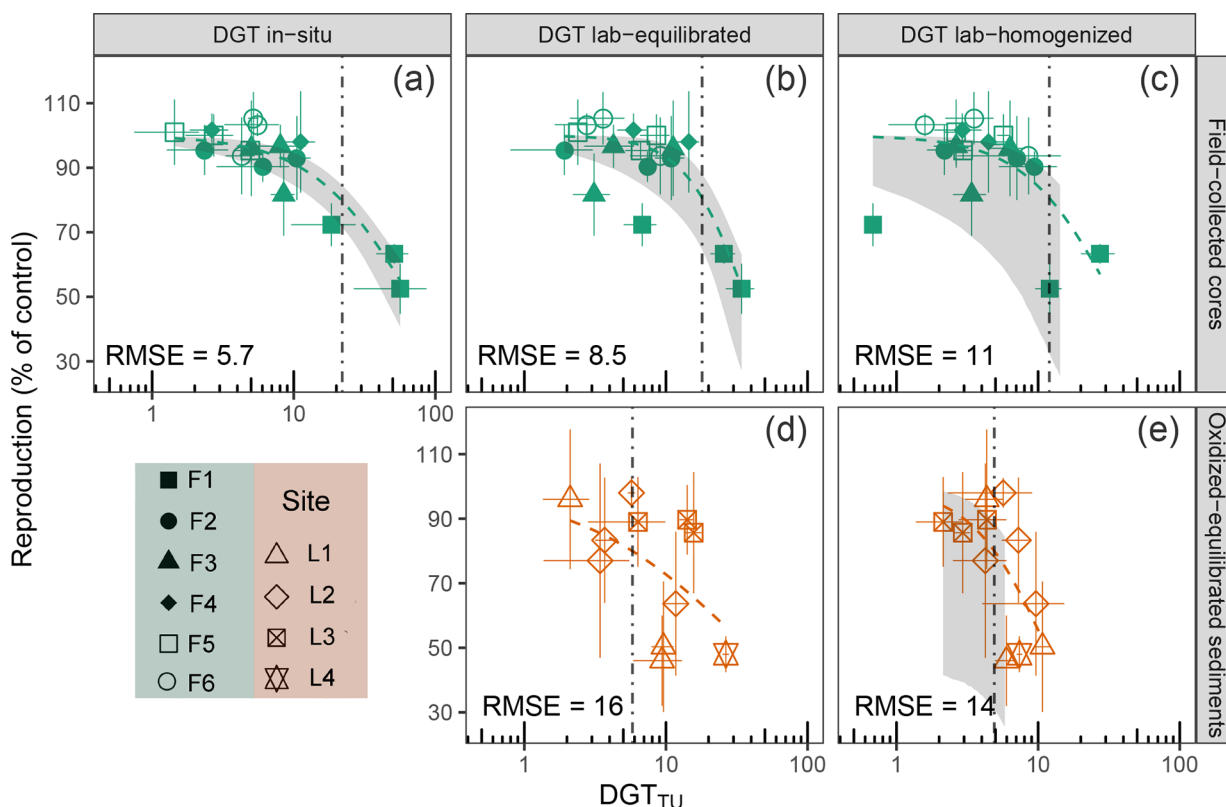


Figure 3. Relationship between toxicity to amphipod reproduction and the DGT_{TU} from different DGT deployment scenarios. Colored dashed lines represent predicted amphipod reproduction using the two-parameter log–logistic model; gray bands are the 95% confidence bands, which are not shown when the lower confidence limits extend beyond the lowest y coordinate. The vertical dotdash lines represent the EC20 simulated using data in each panel.

differences for the three DGT piston deployment scenarios, particularly in the variability of the DGT_{TU} data that influences the performance of the measurements for predicting metal toxicity.

To quantitatively assess the performance of using DGT_{TU} in different deployment scenarios for predicting toxicity, we employed a two-parameter log–logistic model to fit the data. The goodness of fitting of the models was assessed by a root-mean-square error (RMSE) parameter (Figure 3) and by the correlation between observed and predicted amphipod reproduction (SI Figure S6). RMSE ranked in the order of in situ DGT < lab-equilibrated DGT < lab-homogenized DGT (Figure 2a–c), confirming that the in situ DGT_{TU} measurement provided the best bioavailable metal dose-parameter for predicting the magnitude of toxicity. The relationship between predicted and observed toxicity is shown in SI Figure S6 for the three DGT piston deployment scenarios. Correlations between the observed and predicted reproduction indicated consistent goodness-of-fit ranking among different scenarios (SI Figure S6), with the highest correlation in the in situ DGT scenario. For the F1–F6 series, correlation was slightly lower in lab-equilibrated DGT scenario, but lowest when deployed in homogenized sediments.

The effect model enabled the calculation of DGT_{TU} thresholds (representing bioavailable metal fluxes) for sublethal effects on amphipod reproduction: EC10, EC20, and EC50 values. The EC10 values, as well as EC20, were similar between the in situ DGT and lab-equilibrated DGT scenarios (SI Table S3), indicating high consistency in predicting low-metal-toxicity using DGT –metal fluxes derived

in either approach. In contrast, EC50 was higher in the in situ DGT scenario (57 (36–67)) relative to that in lab-equilibrated DGT scenario (36 (23–48)), being also influenced by the slope of dose–response curve that was steeper in the latter scenario. Slope steepening of the curve was attributed to lower metal fluxes, and particularly for DGT_{TU} –Cu, in the lab-equilibrated sediment cores that exhibited the highest toxicity (SI Figures S7–S11). As noted earlier, this may be a result of development of more reducing condition within surface sediments (increasing Fe fluxes, SI Figure S3) and precipitation of metal sulfides that lowers porewater metal concentrations.^{29,68} Possibly for similar reasons, sediment homogenization and short-term equilibration (lab-homogenized) further disturbed the established geochemical equilibrium within the sediments^{27,57} and caused greater variability in the measured fluxes, resulting in increased uncertainty in the dose–response relationship (Figure 3c) and lower EC values with much wider confidence limits (SI Table S3). Therefore, using DGT_{TU} measured in homogenized sediments to predict risks of toxicity was inferior compared with deployments in the field or equilibrated laboratory cores.

In the field-collected sediment cores (F1–F6), a strong dose–toxicity relationship also existed between individual DGT –metal fluxes measured in situ and toxicity for Cu, Zn, Ni, and Pb (panel (a), SI Figures S7–S10). The EC20 values derived from DGT_{TU} for individual metals were 6.0 for Cu, 15 for Zn, and 1.5 for Pb, but <0.1 for Ni (SI Table S4), while noting here the co-occurrence of the metals contributing to the toxicity that results in the individual EC20 values are not being truly independent. Overall, the results indicate that the

impaired amphipod reproduction observed in these intact cores may be attributed mostly to Cu and Zn (Figure 2), while the strong dose–toxicity relationship observed for Ni (SI Figure S9) and Pb (SI Figure S10) may just be due to similar geochemical control of labile Pb and Ni as other metals as indicated by the correlations (SI Figure S5).

3.4. Complexity of DGT_{TU}–toxicity Relationships in Highly Perturbed Sediments. Unlike the toxicity observed in relatively undisturbed field-collected sediment cores (F1–F6), much higher variability was observed in toxicity measured in oxidized and equilibrated sediments (L1–L4) (Figure 3 and SI Figure S12). The average standard deviation of reproduction of the laboratory oxidized–equilibrated sediments was twice the value of the field-collected sediment cores tested a few days after collection in the field ($p < 0.01$, Welch's t test) (SI Figure S12). This suggests that oxidation and equilibration procedures significantly increased the variability in the measured toxic response.

The higher variability in toxicity, as well as that in DGT_{TU} of individual metals (SI Figures S7–S11), obscured the dose–toxicity relationship in laboratory oxidized–equilibrated sediments (Figure 3d,e). RMSE values from the model fitting were both higher than those from the field-collected sediment cores F1–F6 (Figure 3), and consequently the correlations between the predicted and observed toxicity were considerably weaker for the L1–L4 series of oxidation and equilibration treatments (SI Figure S6d,e). Using these weak DGT_{TU}–toxicity relationships, the predicted EC values had very high uncertainties, with 95% confidence intervals beyond the lowest and highest limits in the shown coordinates (and therefore confidence bands are either not shown or incomplete in Figure 3d,e).

While the DGT_{TU} did not adequately predict toxicity in the laboratory oxidized and equilibrated sediments, a strong dose–toxicity relationship existed with DGT_{TU}–Cu as a single individual metal dose parameter, with much lower RMSE values (10.0 and 13.9, SI Figure S7). In contrast, dose–toxicity relationships were not apparent for other individual metals (Zn, Pb, Ni, and Cd) (SI Figures S8–S11, panels d and e). This indicated that labile copper was the dominant cause of the toxicity in these highly perturbed sediments,¹³ and that for these, the inclusion of the other metals obscured DGT_{TU}–toxicity relationships (Figure 3d,e). DGT_{TU}–Zn generally contributed the most to DGT_{TU} in the undisturbed sediments (F1–F6) (Figure 2a–c), and while DGT_{TU}–Zn contributed less in the highly disturbed sediments (SI Figure S13) its relative contribution to the summed toxic unit DGT_{TU} appears not to be simply additive to the measured toxicity.

3.5. Applications and Implications in Contaminated Sediment Assessment. Many current sediment quality assessment practices employ a multiple lines of evidence framework to assess the risk of a contaminated site.^{20,21} However, tiered screening strategies are often utilized initially, that involve first comparing total concentrations of chemicals against SQGVs. If exceeded, more sophisticated investigations are triggered concerning bioavailability, bioaccumulation, toxicity, and benthic ecology. The successful screening in a tiered assessment program may effectively discriminate lower-risk sites from higher-risk sites and lower the overall costs or enable more productive focusing of resources on risk assessment for sites that are more difficult to characterize.

Establishing a linkage between concentrations of chemicals and the degree of adverse effects is often a central task of

sediment quality assessment programs. In relation to linking bioavailable contaminant concentrations to risks of adverse effects, there needs to be confidence in the robustness of the approach, both in relation to collection of the data (application of methods by practitioners) and quality of the line-of-evidence achieved for the assessment. In many assessment settings, in situ toxicity tests are often logistically difficult to undertake, and organism physiology and ecotoxicological responses may be influenced by other stressors, such as variation of temperature, nutrients, and/or flow conditions (both in frequency and duration), all of which may modify biological responses and potentially mask relationships between toxicants and test responses.^{34,69} Therefore, in situ measurement of contaminant lability, as a proxy for bioavailable contaminant concentrations is attractive as a complementary line of evidence (as we seek to achieve with DGT) for both screening and diagnostic purposes for contaminated sites.

In the present study, determination of DGT–metal fluxes measured in situ demonstrated an ability to predict sublethal effects to an epibenthic organism species. Although not able to fully represent the field conditions, the toxicity tests were performed under environmentally realistic conditions, on minimally perturbed field-collected sediment cores in a semiflow-through system that substantially lowered dissolved metal concentrations in the overlying water. The derived EC20 value, with a DGT_{TU} of 20 could be applicable as a conservative guideline value. When in situ DGT measurements of bioavailable fluxes and/or concentrations are not feasible, the application of DGT pistons in field-retrieved sediment cores in laboratory measurements appears to be a useful, although somewhat inferior alternative approach. The present study indicates that DGT measurements from highly disturbed sediments may provide information for some individual metals, including how exposure may change due to disturbance from other metals, but may not be useful when used to determine a DGT_{TU} for combined metals.

Cost-effectiveness and operational expertise are factors that need to be considered when proposing new line-of-evidence for assessment practices. Many improvement recommendations have been ignored because of failing to consider both.³⁴ The use of a significantly cheaper and simpler “piston” DGT probe in the present study achieved a similar level of performance in predicting the toxicity risk of metal contaminated sediments as the much more expensive and specialized “planar” DGT probes (Figure 4). Using these planar probes, Amato et al.¹¹ measured metal fluxes under laboratory conditions within 0.5 cm (above and below) of the SWI for metal contaminated sediments collected from similar metal-contaminated locations as the present study. Although the depth ranges of the metal flux measurement windows were different from those in the present study, both studies showed strong metal flux–toxicity relationships and derived similar EC20 values that have comparable uncertainties (Figure 4). Clearly, the measurement window of a DGT probe controls the source of the metals captured, whether from the overlying water, porewater, or/and labile metals desorbed from sediment particles. The high consistency in metal flux–toxicity relationships observed from different studies highlights the usefulness of DGT pistons applied in situ in prediction of metal toxicity from contaminated surface sediments, regardless of the exposure routes and therefore would ease the application of DGT probes.

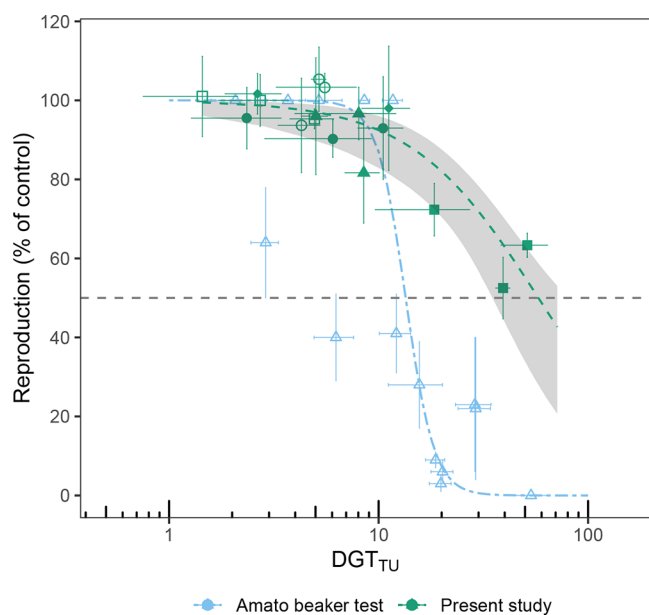


Figure 4. DGT_{TU} with different flux measurement windows (depth ranges) both well predicted the toxicity to amphipod reproduction. DGT -metal fluxes (Amato-beaker test, blue triangles) were measured within 0.5 cm of the SWI,¹¹ while those in the present study (F1–F6) were measured at 0.5–2.5 cm below the SWI.

Overall, this study demonstrated the robustness of relying on in situ measurements using the more cost-effective DGT “pistons” to predict the existence of excessive bioavailable metal concentrations and risks of adverse effects in contaminated sediments. Applying DGT in sediment quality assessments, particularly as an alternative line of evidence for screening purposes, may substantially improve the assessment effectiveness, lower the associated uncertainties, and reduce the overall costs for contaminated site management.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.est.0c07670>.

Details on the field operation, sediment collection, laboratory sediment treatment, toxicity test procedures, sampling and chemical analysis, and QA/QC results; physical and chemical properties of sediments from different sites; distribution of DGT labile metal fluxes; correlations between predicted and observed amphipod reproduction; relationship between toxicity and individual DGT-metal fluxes (PDF)

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Notes

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■ DEDICATION

The authors dedicate this research to Peter Teasdale, who passed away suddenly on August 7, 2020.

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